Monte Carlo Computer Simulations of Irreversible Adsorption of Colloid Particle at Solid-Liquid Interface

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Colloid dispersion is a multi-phase system composed of a medium that can be considered continuum, in which one or more phases (particles) are dispersed. In our research we focus on systems containing a liquid medium (usually water or electrolyte) and solid or liquid particles. By definition, colloid particle size is of the order of 1 – 1000 nm. Simple geometrical considerations suggest that the surface to volume ratio calculated for any body is inversely proportional to the body's linear dimensions. Therefore, because of a very small particle size, colloid dispersions are systems, which have an extremely large interfacial area between two of the phases: media and colloidal particles. In such systems surface effects, such as electrostatic interaction between charged particles' surfaces, play much more important role than volume effects, e.g., gravity. This results in several characteristic properties of colloids. First, larger colloid particles scatter a light beam passing through them (Tyndall effect) due to reflection of the light by their surfaces. Next, because of their small mass, the particles undergo a random motion in a suspension due to collisions with small, invisible, fast moving solvent molecules (Brownian motion). Another interesting feature is the electrostatic charge effect, which consists in spontaneous charging of colloid particles in a polar media like water. The origin of the charge may be adsorption of ions from the solution or dissociation of ionogenic groups at the particles' surfaces. Finally, due to their big surface area, colloids have a great adsorbing power.

Colloid dispersions are very common in nature and industry. An important example is blood containing many bio-molecules and cells. Other common examples are milk, inks, paints, and wastewater. Very often we are interested in collecting colloid particles at a solid surface. This may be either because we want to remove them from a suspension (e.g., wastewater filtration) or we need themselves for a further processing or application (e.g., enzymes immobilization). The phenomenon of collecting of colloid particles at a solid-liquid interface, called adsorption, has a great significance in many natural and practical processes such as membrane filtration, paper making, protein and cell separation, biofouling of membranes, organ transplantation, and many other. Experimental observations of adsorbed colloid particles suggest that their adsorption is usually irreversible and localized, that means attached particles can not desorb or move at the collector surface even at a strong hydrodynamic flow. Again, it is a consequence of the large surface to volume ratio, which makes the electrostatic particle-interface attractive interaction much stronger than hydrodynamic forces.

Irreversible colloid adsorption can be modeled using a variety of approaches. Among them, the Monte Carlo random sequential adsorption (MC-RSA) approach seems to be the most suitable because of its simplicity and efficiency. The classical RSA model [1] considers a sequence of trials of monodisperse, spherical particle adsorption at a homogeneous interface, taking into account geometrical effects only. The simulation loop consists of the following steps:

1. a virtual (adsorbing) particle is created through choosing at random its x and y coordinates on the square simulation plane with periodic boundary conditions at its perimeter
2. then, the adsorbing particle's vicinity is scanned to determine the minimum interparticle distances
3. if the virtual particle overlaps with any of previously adsorbed particles the adsorption trial is rejected and the particle is permanently removed from the system
4. otherwise, the particle is assumed irreversibly adsorbed and its coordinates are stored

The process is continued until the entire surface is completely covered and no more particles can be accommodated thus the maximum (jamming) coverage is attained.

Since the 1980s a number of extended RSA models have been developed that include the effects of particle shape [2], Brownian motion [3], external force [4], particle-particle and particle-interface electrostatic interaction [5], colloid-particle polydispersity [6], and surface heterogeneity [7]. Recently, the simulation algorithm has even been extended for multilayer adsorption simulations [8]. The results based on RSA simulations allow us to predict particle layer structure and the jamming

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coverage of particles. We can use the model to predict particle-adsorption kinetics as well, although, depending on the particle-transport mechanism, an appropriate analysis of real adsorption problems can require including a correction for bulk transport or the hydrodynamic scattering effect. Thus, RSA modeling can be a powerful tool in the study of irreversible adsorption of macromolecules, proteins, and colloid particles.
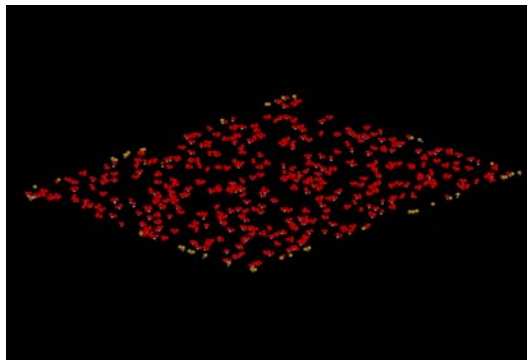

Fig.1. Adsorbed colloid particle "monolayer" close to jamming simulated numerically at a random site (heterogeneous) surface. Note that the large colloid particles (red) are adsorbed only on the small, white spheres representing active sites or heterogeneities. Large to small particle size ratio equals two. Blue and yellow spheres represent heterogeneities and colloid particles located at the boundary layer (at the surface perimeter) that were periodically replicated.

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